

Motion in Crystals: The Molecular Mean Field Model

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Abstract

The problem of describing collective atomic motion in molecular crystals is reviewed from the point of view of normal coordinate analysis in its mean square amplitude form. There are two related problems with this approach: (1) The apparent lack of information on correlation between atomic motion inherent in atomic displacement parameters as determined from elastic diffraction experiments. (2) The need to identify molecular deformation coordinates associated with low frequencies and therefore with large amplitudes. Within the limits of the harmonic approximation the first problem can be solved by considering mean square amplitudes obtained at different temperatures. The second problem can be approached by analyzing and visualizing the deviations of atomic displacement parameters from rigid body behavior or, alternatively, by looking for static deformations of molecular fragments closely related in structure to the molecule whose atomic displacement parameters are to be analyzed. Some of the above points are illustrated with the help of the atomic displacement parameters of $\text{H}_8\text{Si}_8\text{O}_{12}$, determined at 100 and 10 K.

1. Introduction

The notion that crystals are regular and undeformable arrangements of motionless atoms or of rigid and immobile molecules is no more than a crude first approximation to the description and understanding of the crystalline state of matter. Upon closer inspection at the microscopic level, a rich spectrum of diverse types of motion becomes apparent. These motions include all that are also observed in the liquid and gaseous states: chemical reaction, diffusion, rotation, translation and vibration, albeit with characteristic differences between the different phases. Correspondingly, the experimental techniques used to investigate these motions are similar in all phases (Braga, 1992): mainly spectroscopy and diffraction, inelastic as well as elastic.

All motion has two aspects: the displacements of the moving particles in space on the one hand and the energies (or corresponding time scales) associated with them on the other. Spectroscopic and inelastic diffraction experiments probe primarily the energetic aspects of motion, *i.e.* its eigenvalue spectrum, whereas elastic diffraction experiments probe atomic positional displacements, *i.e.* the eigenvector characteristics of motion. The denominator common to both of these aspects is the energy surface governing the motion.

Here we shall concentrate on atomic positional displacement parameters in the crystal, specifically their interpretation in terms of internal, librational and translational vibrations of molecules. We shall deal with these matters from the point of view of vibrational analysis and attempt to relate the interpretation of IR and Raman spectra in terms of interatomic forces, with a corresponding analysis of atomic displacement parameters from elastic diffraction experiments. The various difficulties inherent in this approach and solutions to them are reviewed, and illustrated with an example.

The information on atomic displacements in crystals is usually derived from interpretations of elastic or Bragg diffraction experiments using X-rays or neutrons. It is assumed that the crystal is built from atoms which are characterized by their electron or nuclear density at rest, their most probable or mean position \mathbf{x}_0 and a probability density function (p.d.f.) describing displacements from this position in a harmonic or anharmonic potential. It is common and often sufficient to assume an anisotropic harmonic potential which implies an anisotropic Gaussian form for the p.d.f.

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$$\text{p.d.f.}(\mathbf{x} - \mathbf{x}_0) = (2\pi)^{-3/2} (\det \mathbf{U}^{-1})^{1/2} \times \exp[(\mathbf{x} - \mathbf{x}_0)^T \mathbf{U}^{-1} (\mathbf{x} - \mathbf{x}_0) / 2]. \quad (1)$$

Here \mathbf{U} is the well known anisotropic displacement tensor; the diagonal components are the mean square displacements along the unit-cell axes and the off-diagonal elements are related to the correlation c_{ij} of simultaneous displacements along pairs of axes

$$c_{ij} = U_{ij} / (U_{ii} U_{jj})^{1/2}. \quad (2)$$

A list of anisotropic displacement parameters, *i.e.* of the elements of \mathbf{U} , is only slightly more informative than a list of atomic coordinates. Coordinates themselves do not provide direct information on the mutual interactions of atoms. The chemical interpretation of atomic coordinates is a relatively simple matter, however, since it is based on a straightforward transformation to bond distances, angles and other chemically meaningful coordinates which may be easily compared with each other and with results from models such as quantum chemical calcula-

tions. Although anisotropic displacement parameters describe the degree and direction of motions of individual atoms, they provide little information on interatomic interactions, *i.e.* on cooperative atomic displacements in the crystal and the forces associated with them.

2. Ways of looking at motion in crystals

Given this deficiency of the anisotropic displacement parameters, it is useful to survey several methods of studying atomic motion in crystals. Adopting the most general point of view, a crystal is considered as a giant molecule composed of a large number of (atomic) particles – of the order of Avogadro's number – and with macroscopic dimensions. Each atom may interact – to varying degrees – with all others, or at least with a large number of its neighbors located within a certain distance (*e.g.* 10 Å). Describing the dynamics of such a system is a formidable problem, which is only somewhat alleviated by taking translational and other symmetries of the crystal into account. The theory of lattice dynamics provides the necessary physical and mathematical models (see, for example, Willis & Pryor, 1975; Decius & Hexter, 1977). It is used mainly to interpret inelastic neutron scattering experiments; its practical application is limited to crystal structures with fairly small unit cells, typically ionic and molecular compounds containing one or a few dozen atoms at most.

At the other extreme, only a single atom is considered. This atom is assumed to move in the average potential field of all of its neighbors. This is known as the atomic mean field model (a.m.f.m.); it is the basis of all descriptions of atomic motion in terms of harmonic and anharmonic, isotropic and anisotropic displacement parameters commonly being used to interpret elastic diffraction experiments.

Many crystal structures can be considered as being built from discernable entities – molecules. In these crystals interatomic interactions may be divided into strong ones, those within molecules, and weaker ones between molecules. This suggests the possibility of considering a model of intermediate complexity, *i.e.* motions of a flexible molecule in the averaged environment of all neighboring molecules in the crystal. Such a model is more informative – and also more complicated – than the atomic mean field model but less general – and substantially simpler – than the lattice dynamical one. In analogy to the a.m.f.m., it may be named the molecular mean field model (m.m.f.m.). The necessary physical and mathematical theory – discussed below – is closely related to the well known theory of molecular normal coordinate analysis (Wilson, Decius & Cross, 1955).

To set the stage, the motions of a molecule in the molecular mean field are compared with those of an isolated molecule. The isolated molecule translates and rotates freely, whereas a molecule in the crystal –

constrained by its environment – performs translational and librational oscillations about its equilibrium position and orientation. In both cases the molecule undergoes intramolecular motions, including rotation about bonds, deformation of bond angles and bond distances or a combination of these. In a free molecule these motions are the result of intramolecular interatomic interactions only, whereas in the crystal these interactions may be modified to a larger or smaller extent by the molecular environment, the molecular mean field. All these motions imply correlated displacements of several or all the atoms and yet, as pointed out above, the anisotropic displacement parameters from elastic diffraction experiments provide no direct information about these correlations. What can we do?

3. Retrieving the missing information

As mentioned in the *Introduction*, there are basically two methods of analyzing motion: one is based on energy, *i.e.* on normal coordinate analyses of vibrational frequencies (Wilson, Decius & Cross, 1955), the other on displacements, *i.e.* on normal coordinate analysis of mean square amplitudes (Cyvin, 1968). The problem of insufficient information is encountered in both, albeit in different guise. An overview of the two approaches, of their relationship, of their inherent problems and of the approximations employed to overcome them may therefore be instructive.

3.1. Normal coordinates from vibrational spectroscopy

The energy required for atomic displacements x_i from equilibrium is, in harmonic approximation

$$V = 1/2 \sum_i \sum_j x_i x_j f_{ij} = \mathbf{x}^T \mathbf{f} \mathbf{x} / 2, \quad (3)$$

where f_{ii} are the force constants for the displacement of a given atom in a given direction and f_{ij} are the interaction constants for simultaneous displacements of an atom in more than one direction or of more than one atom in the same or different directions. The observable frequencies ν_k are related to the force constants through the eigenvalue problem

$$|\mathbf{f} \mathbf{m}^{-1} - \lambda \mathbf{I}| = 0, \quad (4)$$

where \mathbf{f} is the symmetric matrix of force constants f_{ij} , \mathbf{m} is a diagonal matrix of atomic masses m_i , \mathbf{I} is the identity matrix and λ is a vector with elements $4\pi^2 \nu_k^2$ (in s^{-2}). Equation (4) serves the purpose of calculating the force constants from the observed frequencies (Wilson, Decius & Cross, 1955, Ch. 2).

There is a problem, however: for an n -atomic molecule the number of unknown independent elements f_{ij} is, in general, $3n(3n+1)/2$ [or $(3n-6)(3n-5)/2$ if rotation and translation are unconstrained], whereas the number

of observable frequencies is only $3n$ (or $3n - 6$). Thus, the problem of calculating f_{ij} from ν_k is heavily underdetermined. The chemical solution to the problem is to measure the spectra of a large number of isotopically substituted molecules with different ν_k , different m_i but identical f_{ij} . Given a sufficient number of observed frequencies, the force constants can be determined.

The method of isotopic substitution is laborious and – in practice – often insufficient to solve (4). In such cases the force constant matrix \mathbf{f} can be determined only approximately. There are many types of approximations, mostly based on empirical chemical considerations. In most of these cases, the problem is transformed from positional to some type of chemical deformation coordinate p_i . The potential energy for molecular deformation is now

$$V = 1/2 \sum_i p_i p_j F_{ij} = \mathbf{p}^T \mathbf{F} \mathbf{p} / 2. \quad (5)$$

The elements F_{ii} are the force constants for bond stretching, angle deformation, *etc.* F_{ij} are interaction constants. \mathbf{F} is related to the frequencies through an eigenvalue problem, popularized by Wilson, which is analogous to (4) (Wilson, Decius & Cross, 1955, Ch. 4)

$$|\mathbf{F} \mathbf{G} - \lambda \mathbf{I}| = 0. \quad (6)$$

\mathbf{G} depends only on the known geometric arrangement of the atoms and on their masses. An approximate solution to this equation is obtained by judiciously identifying elements of \mathbf{F} , *e.g.* from symmetry and chemical considerations, which are known or suspected to be equal, or zero, or small. In this way, the number of unknowns is reduced and the symmetric $3n \times 3n$ matrix \mathbf{F} can often be factored into small subproblems which are correspondingly easier to solve.

3.2 Mean square amplitudes from normal coordinates

Solving (4) leads not only to the force constants f_{ij} , but also to eigenvectors \mathbf{I}_k^x for each normal mode k (Cyvin, 1968). The matrix \mathbf{I}^x of eigenvectors obeys the condition

$$\mathbf{I}^x (\mathbf{I}^x)^T = \mathbf{m}^{-1}. \quad (7)$$

The elements I_{ik}^x represent the relative displacement of atom i in mode k . They are proportional to the absolute atomic displacements u_{ik} . The temperature-dependent proportionality factor is $[(h/8\pi^2\nu_k)\coth(h\nu_k/2kt)]^{1/2}$. From the atomic displacements it is only a small step to anisotropic displacement parameters. The mean square amplitudes attributable to a single normal mode are

$$\Sigma_{ijk}^x = u_{ik} u_{jk}. \quad (8)$$

The total mean square amplitudes Σ_{ij}^x are simply the sum over all normal modes. Due to the reciprocal dependence on ν_k , the largest contributions to Σ_{ij}^x are from the vibrations with the smallest frequencies.

The resulting Σ^x -matrix is symmetric and of the dimensions $3n \times 3n$. It is best considered to be built from n^2 (3×3) blocks, with n on the diagonal of Σ^x and the remainder in off-diagonal positions. The n diagonal blocks are nothing other than atomic mean square displacement tensors \mathbf{U} , which can also be obtained directly from elastic diffraction experiments; the off-diagonal blocks contain the information on correlations of motion between atoms and are not obtainable from elastic diffraction. Note that Σ^x is temperature dependent, as are the u 's.

3.3 Normal coordinates from mean square amplitudes

Given the fact that the mean square amplitudes may be obtained from vibrational frequencies *via* an intermediate determination of force constants, the question arises whether the reverse is also possible, *i.e.* to determine the frequencies and force constants from mean square amplitudes. The answer is yes and there are close analogies between the two approaches (Cyvin, 1968). Most importantly, there is an analogous eigenvalue equation

$$|\Sigma^x \mathbf{m} - \delta \mathbf{I}| = 0, \quad (9)$$

where δ is a vector with elements $(h/8\pi^2\nu_k)\coth(h\nu_k/2kt)$.

The problem is again of the dimensions $3n \times 3n$. In an elastic diffraction experiment the unknown quantities are the off-diagonal (3×3) blocks of Σ^x , with $3n(3n - 1)/2$ independent elements and the $3n$ frequencies ν_k . The observable quantities are the atomic anisotropic displacement parameters, *i.e.* the diagonal (3×3) blocks of Σ^x , only $6n$ in all. Thus, this is another case of heavy underdetermination and (9) can be solved only approximately. The methodology is analogous to that described in §3.1. It relies on chemical coordinates and the appropriate simplifications. The corresponding eigenvalue equation is (Cyvin, 1968)

$$|\Sigma \mathbf{G}^{-1} - \delta \mathbf{I}| = 0. \quad (10)$$

The elements of Σ are the mean square amplitudes of libration, translation and internal motions. Σ and Σ^x are related by the transformation

$$\Sigma^x = \mathbf{A} \Sigma \mathbf{A}^T. \quad (11)$$

The transformation matrix \mathbf{A} depends only on the known geometry of the molecule. Each of its elements relates an internal to an atomic displacement coordinate. In general, Σ^x and Σ are of the dimensions $3n \times 3n$. In practice, however, only a small number of internal coordinates are considered, those involved in the normal vibrations of low energy and associated with large mean square amplitudes. Thus, similar to the case of the determination of \mathbf{F} , where judiciously selected elements F_{ij} are assumed to be zero, here some elements Σ_{ij} are neglected. This

affects the transformation (11) as follows (Fig. 1). As mentioned above, Σ^x contains the anisotropic displacement parameters U_i, \dots, U_n on the diagonal. The matrix Σ of internal mean square displacements is divided into four parts: $T, L, \Sigma_{pp}, \Sigma_{qq}$ and the corresponding off-diagonal blocks S, Σ_{lp} etc. T, L and S contain the mean square amplitudes of translation, libration and screw coupling well known from rigid body analysis (Schomaker & Trueblood; 1968); Σ_{pp} contains the mean square amplitudes for the internal coordinates p with large amplitude motions; Σ_{lp} and Σ_{lp} are the coupling tensors between libration, translation and internal motion. Finally $\Sigma_{qq}, \Sigma_{lq}, \Sigma_{lq}$ and Σ_{pq} are associated with the motions that are known or assumed to be small. Matrix A can be subdivided correspondingly. Provided that the r important internal coordinates can be identified, transformation (11) takes the modified form

$$\Sigma^x = A' \Sigma' (A')^T. \quad (12)$$

Σ' is now of the dimensions $r \times r$, and A' is of the dimensions $3n \times r$ since all elements of Σ and A associated with q are assumed to be zero.

Most schemes of interpreting anisotropic displacement parameters attempt to determine $r(r+1)/2$ independent elements of Σ' from the $6n$ observable elements of Σ^x . This is usually achieved by a least-squares calculation with the minimizing conditions

$$\frac{\partial}{\partial \Sigma'_{st}} \sum_{i \geq j} \{ \Sigma^x_{ij} - [A' \Sigma' (A')^T]_{ij} \}^2 w_{ij} = 0, \quad (13)$$

where Σ^x_{ij} are the components of the anisotropic displacement parameters U , w_{ij} is a weight, and Σ'_{st} are the determinable elements of Σ' . Equations (12) and (13) are general and apply to any combination of translational, librational and internal displacements (He & Craven, 1985, 1993). In the simple case where only translation and libration are considered, $r = 6$ and the transformation A' is identical to E as given by Johnson (1970a), and is related to the arrays H and G in the treatment of Schomaker & Trueblood (1968).

The cases of internal rotation about single bonds or translational oscillation of one part of a molecule relative to another have been discussed in some detail. In both cases it is usually assumed that internal motion affects

only the rotating (Dunitz & White, 1973; Johnson, 1970b) or translating group (Bürgi, 1989). Thus, internal motion is associated with an angular or linear momentum of the molecule as a whole and is therefore not orthogonal to overall libration and translation. In terms of the above formalism, the columns A_p of A referring to internal rotation or translation are no longer orthogonal to those referring to overall rotation or translation. This complication has been avoided by He & Craven (1985, 1993).

In practice, the least-squares determination of Σ' is beset with a number of difficulties. A well known one is the indeterminacy of the trace of S in rigid body analysis (Schomaker & Trueblood, 1968). As internal coordinates are added to the model, additional indeterminacies, primarily in the Σ_{lp} and Σ_{lp} couplings, have to be dealt with (Schomaker & Trueblood, 1984; Bürgi, 1989). A common approximation is to assume that some or all of these coupling elements are zero [see Dunitz & White (1973), He & Craven (1985, 1993)].

In view of these shortcomings, it is preferable to interpret anisotropic displacement parameters on the basis of (9) and (10), provided, of course, that sufficient experimental information is available. One possibility is to introduce spectroscopic measurements, *i.e.* some elements of δ . Second, one may resort to the temperature dependence of the elements of Σ^x and Σ , *i.e.* solve (9) using anisotropic displacement parameters measured at different temperatures, as will be discussed in more detail below. There are problems with both these possibilities: Measured IR and Raman frequencies (pertaining to the origin of the Brillouin zone) may not be representative of the frequencies corresponding to the molecular mean field (which are some type of average over the entire Brillouin zone) and the mean field in a real crystal may be neither completely harmonic nor completely independent of temperature. We are not aware, however, of any serious attempt at solving (9) along the two lines suggested above.

As an example, the full determination of the elements of T, L and S (and, therefore, of the trace of S) is sketched. At any temperature t

$$R'(t) = \begin{bmatrix} T(t) & S(t) \\ S^T(t) & L(t) \end{bmatrix} = I^i \delta(t, \nu_k) (I^i)^T. \quad (14)$$

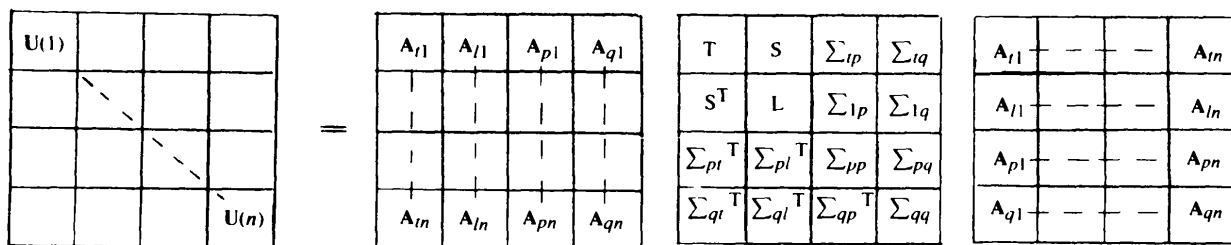


Fig. 1. Transformation from internal mean square amplitudes Σ to positional mean square amplitudes Σ^x ($\Sigma^x = A \Sigma A^T$). The matrices A and Σ are partitioned into blocks corresponding to molecular translation (t), libration (l) and internal motion (p and q ; see text).

The matrix \mathbf{I}^i contains the eigenvectors associated with the diagonal matrix of eigenvalues $\delta(t, \nu_k)$. Both \mathbf{I}^i and ν_k are temperature independent; \mathbf{I}^i has to obey the side condition

$$\mathbf{I}^i(\mathbf{I}^i)^T = \mathbf{G}, \quad (15a)$$

and is related to \mathbf{I}^x through

$$\mathbf{I}^x = \mathbf{A}^i \mathbf{I}^i. \quad (15b)$$

Equation (15a) provides 21 conditions among the 36 unknown elements of \mathbf{I}^i . Together with the six frequencies ν_k there are 21 unknowns to be determined from the 20 independent elements of $\mathbf{T}(t)$, $\mathbf{L}(t)$ and $\mathbf{S}(t)$ (Schomaker & Trueblood, 1968). With data from a single temperature, (14) is underdetermined. If data at more than one temperature are available, the number of observations exceeds the number of unknowns which is still the same. To see how this works it is necessary to consider the dependence of $\delta_k(t, \nu_k) = h/8\pi^2\nu_k \coth(h\nu_k/2kt)$ on temperature. At absolute zero there is no dependence, $\delta_k = h/8\pi^2\nu_k$; in the high-temperature classical limit, when $2kt \gg h\nu_k$, there is a linear dependence, *i.e.* $\delta_k(t, \nu_k) = kt/4\pi^2\nu_k^2$. Analogous arguments apply to Σ and Σ^x . The effect of all this is that the elements of δ_k , Σ and Σ^x increase by different factors between the low- and high-temperature regimes (Fig. 2). As a consequence, the principal values of the anisotropic displacement parameters may also increase by different factors and their principal directions (eigenvectors), *i.e.* the orientation of the equiprobability ellipsoids [see §3.4, (19)], may change. It is important, therefore, that at least one determination of Σ or Σ^x be made at sufficiently low temperature for which the functions $\delta_k(t, \nu_k)$ are not in their classical linear regime; if they were, observational equations (14) at different t would be proportional to t itself, *i.e.* linearly dependent, and no

new information would be gained. These arguments should also be applicable to the determination of those elements in Σ_{ip} , Σ_{ip} and Σ_{pp} which are not obtainable from data at a single temperature (Schomaker & Trueblood, 1984; Bürgi, 1989).

From the discussion in this section the following conclusions may be drawn: (1) A basis for the interpretation of anisotropic displacement parameters in terms of collective intramolecular motion of atoms in molecular crystals is provided by the theory of normal coordinate analysis in its mean square amplitudes form and its molecular mean field approximation. (2) There are two main problems in such analyses. The first is to find the relevant internal coordinates, *i.e.* those with low force constants, involved in low vibrational frequencies and with correspondingly large amplitudes of vibration. The second problem is that at a given temperature the atomic anisotropic displacement parameters alone are insufficient for a normal coordinate analysis or, expressed differently, that not all of the necessary internal mean square amplitude quantities are determinable from the available anisotropic displacement parameters, even if only a limited number of relevant internal coordinates is considered. Most of these problems have not been studied in a general and systematic way. (3) The outline in this section suggests experiments which may help to solve some of the above problems and which, to the best of our knowledge, have not been seriously pursued. These experiments include studying the effects of temperature on the orientation and magnitudes of the anisotropic displacement parameters, as well as the simultaneous interpretation of anisotropic displacement parameters and vibrational frequencies, *i.e.* of geometrical and energetic observables.

3.4. Identifying molecular flexibility in general and the relevant internal coordinates in particular

As indicated above, interpretation of anisotropic displacement parameters in the absence of spectroscopic or other nondiffraction information requires some knowledge about the types of low-energy motions which account for the major part of the anisotropic displacement parameters. It is usually assumed that translation and libration are among these. There are various methods to test for additional internal motion. One method is the rigid molecule test (Rosenfield, Trueblood & Dunitz, 1978) based on Hirshfeld's rigid bond test (Hirshfeld, 1976). It makes use of the fact that for a rigid molecule, performing translation and libration only, the mean square amplitudes of any pair of atoms in a molecule along their internuclear unit vector \mathbf{n}_{ij} are equal, *i.e.* their difference is zero

$$\Delta U_{ij} = \mathbf{n}_{ij}^T (\mathbf{U}_i - \mathbf{U}_j) \mathbf{n}_{ij} = 0. \quad (16)$$

For a significant deviation from zero, there must be internal motion. It is not always easy, however, to define

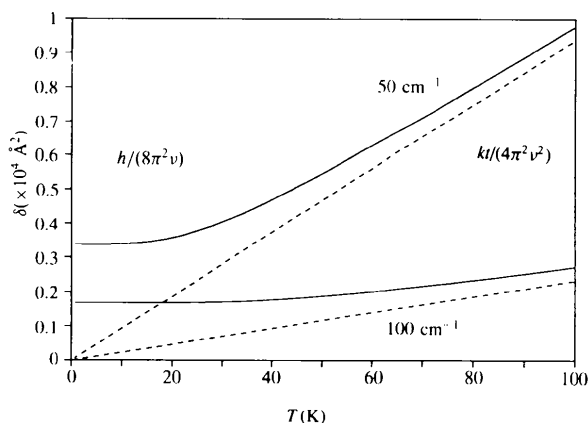


Fig. 2. Temperature dependence of $\delta(t, \nu_k) = h/8\pi^2\nu_k \coth(h\nu_k/2kt)$. The zero-point mean square amplitude per mass unit is $\delta(0, \nu_k) = h/8\pi^2\nu_k$. In the high-temperature classical regime ($kt > h\nu_k$) $\delta \approx kt/4\pi^2\nu_k^2$. The plot shows δ in units of 10^{-4} \AA^2 for $\omega_k = \nu_k/c$ of 50 and 100 cm^{-1} (c : velocity of light).

the nature of the internal coordinates from the ΔU 's alone.

A second method of testing for internal motion is to perform a rigid body analysis and to analyze the residual tensors

$$\Delta U = U_{\text{obs}} - U(\text{rigid body}). \quad (17)$$

If they are significant, the presence of intramolecular motion is indicated, but as in the case of ΔU_{ij} its nature may not be obvious.

Both the above methods have additional shortcomings. The rigid molecule test provides incomplete information for planar molecules. It produces $n(n-1)/2$ quantities, which are difficult to visualize. Similarly, rigid body analysis yields n difference tensors ΔU , $6n$ quantities in all. In order to facilitate their interpretation, we have developed the graphics program *PEANUT* (Hummel, Hauser & Bürgi, 1990), which allows to visualize mean square amplitude or root mean square amplitude surfaces (Nelmes, 1969) and corresponding difference surfaces

$$\Delta U(\mathbf{n}) = \mathbf{n}^T \Delta U \mathbf{n} \quad (18a)$$

$$[\Delta U(\mathbf{n})]^{1/2} = [\mathbf{n}^T \Delta U \mathbf{n}]^{1/2}, \quad (18b)$$

where \mathbf{n} is a unit vector whose direction is systematically varied over the surface of a sphere.

This representation is necessary because the difference tensors ΔU , unlike the U 's themselves, are often nonpositive definite and can therefore not be represented as an equiprobability surface

$$\mathbf{x}^T \Delta U^{-1} \mathbf{x} = \text{const}, \quad (19)$$

since they would take the form of open hyperbolic functions rather than closed equiprobability ellipsoids. Surfaces according to (18) are always closed. Visual inspection of the pictorial representation of ΔU 's can provide an indication of the relevant internal motions. Several examples have been discussed elsewhere (Hummel, Raselli & Bürgi, 1990).

An entirely different method for identifying low-energy internal coordinates uses statistical analysis of atomic coordinates. Molecular fragments closely related to the molecule whose anisotropic displacement parameters are to be analyzed are retrieved from the Cambridge Structural Database (CSD). Their equilibrium structures are compared and the principal deformations from a mean reference structure identified by principal component analysis (Taylor & Allen, 1994). The most important principal components may then be taken as models for the soft deformation coordinates (Bürgi & Dunitz, 1994) and introduced into the analysis of anisotropic displacement parameters.

4. An example, $\text{H}_8\text{Si}_8\text{O}_{12}$

The tests outlined in §3.4 will now be illustrated for the spherosiloxane molecule $\text{H}_8\text{Si}_8\text{O}_{12}$ (Fig. 3). $\text{H}_8\text{Si}_8\text{O}_{12}$

may be considered as a molecular model of one of the secondary zeolitic building blocks, consisting of a cube of eight Si atoms, whose 12 edges are bridged by O atoms and whose corners are substituted by H atoms. The crystallographic site symmetry is $\bar{3}$, but the molecular structure is very close to $m\bar{3}$ symmetry. If it were not for the O atoms which are *ca* 0.1 Å displaced from the diagonal mirror planes of the silicon cube, the molecule would show $m\bar{3}m$ symmetry (Auf der Heyde, Bürgi, Bürgi & Tömroos, 1991).

4.1. $\text{H}_8\text{Si}_8\text{O}_{12}$ is a flexible molecule

ΔU 's between Si and O determined at 100 and 10 K are listed in Table 1; they have been singled out, because they are the most revealing. Averaging with respect to the approximate $m\bar{3}$ symmetry, there are 1,2-differences along the Si—O bonds, two types of nonbonded 1,4-differences and one type of 1,6-difference. Except for the bonded 1,2-differences, ΔU 's are all highly significant, indicative of intramolecular motion in $\text{H}_8\text{Si}_8\text{O}_{12}$. The value for the Si—O bond is practically temperature independent, as expected for a high-energy stretching coordinate; those for the nonbonded contacts decrease by 55% on lowering the temperature, as expected for low-energy coordinates.

The rigid body analysis on $U(\text{Si})$ and $U(\text{O})$ gives goodness-of-fit (GOOF) values of 22 (100 K) and 49 (10 K). The L and T tensor elements show large e.s.d.'s (Table 2). The diagonal elements of $\Delta U(\text{Si})$ are consistently negative, those of $\Delta U(\text{O})$ are positive. The large GOOF values and the systematics in ΔU both indicate the presence of internal motion.

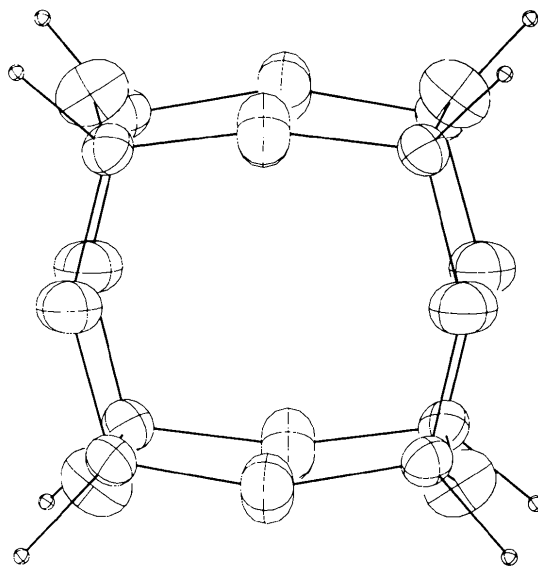


Fig. 3. Observed anisotropic displacement parameters of $\text{H}_8\text{Si}_8\text{O}_{12}$ at 100 K; root mean square amplitudes surfaces $2.5(\mathbf{n}^T U(\text{obs}) \mathbf{n})^{1/2}$ [see equation (18b)]. H atoms are given in arbitrary size.

Table 1. Observed and calculated values ΔU_{SiO} along internuclear vectors

$d(\text{Si—O})$ at 100 K (Å)	$\Delta U(100\text{ K}) (\times 10^4 \text{ \AA}^2)^*$		$\Delta U(10\text{ K}) (\times 10^4 \text{ \AA}^2)^\ddagger$	
	obs [†]	calc	obs [†]	calc
1.62	1 (1)	4	-2 (1)	4
3.71	82 (6)	81	38 (2)	37
3.83	65 (5)	66	28 (3)	31
5.08	68 (2)	68	34 (2)	33

* Data from Auf der Heyde, Bürgi, Bürgi & Törnroos (1991).

† Averaged with respect to $m\bar{3}$ symmetry, e.s.d. of the population.

‡ Data from Törnroos (1994).

Fig. 4 shows a PEANUT plot of $[\Delta U(\text{Si})]^{1/2}$ and $[\Delta U(\text{O})]^{1/2}$ at 100 K. Two observations can be made immediately: (1) Oxygen shows excess motion (relative to the rigid body model) in the direction perpendicular to the Si—O—Si plane and along the Si—O—Si bisector, but not along the Si—O bond. (2) The pattern of ΔU 's shows noncrystallographic $m\bar{3}$ symmetry in good approximation, indicating that the intramolecular motion is largely dictated by the approximate molecular and not by the crystallographic symmetry. From the picture it is seen that angle bending at oxygen and torsion about the Si—O bonds may be important, but we have no idea how the 12 bending and the 24 torsional coordinates are correlated.

Thus, as a next step, the structures of 16 Si_8O_{12} fragments were retrieved from the CSD and analyzed for distortions from a reference structure of $m\bar{3}m$ symmetry, the highest symmetry the Si_8O_{12} fragment can attain.

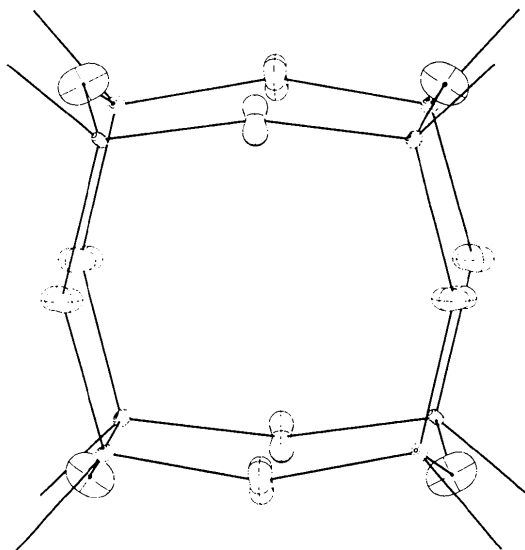


Fig. 4. Residual anisotropic displacement parameters of $\text{H}_8\text{Si}_8\text{O}_{12}$ at 100 K after subtraction of translational and librational contributions; root mean square amplitude surfaces $2.5[\mathbf{n}^T(\mathbf{U}(\text{obs}) - \mathbf{U}(\mathbf{T}, \mathbf{L}\mathbf{n}))^{1/2}]$ [see equation (18b)]. Solid lines: positive difference; broken lines: negative difference. Note the negative residuals at Si and the oblate shape of the positive residuals at O.

Table 2. Translation and libration tensor of $\text{H}_8\text{Si}_8\text{O}_{12}$ at 100 and 10 K (a) from \mathbf{U}_{obs} and (b) from \mathbf{U}_{obs} after correction for internal motion

100 K	(a)	(b)
$L_{11} = L_{22}$ (deg ²)	1.4 (7)	1.88 (5)
L_{33} (deg ²)	1.7 (1.1)	1.81 (7)
$T_{11} = T_{22}$ (Å ²)	0.0091 (15)	0.0058 (1)
T_{33} (Å ²)	0.0090 (15)	0.0057 (1)
GOOF	22.3	1.8
10 K		
$L_{11} = L_{22}$ (deg ²)	0.3 (3)	0.64 (5)
L_{33} (deg ²)	0.5 (5)	0.74 (6)
$T_{11} = T_{22}$ (Å ²)	0.0047 (6)	0.0024 (1)
T_{33} (Å ²)	0.0052 (6)	0.0028 (1)
GOOF	48.6	7.6

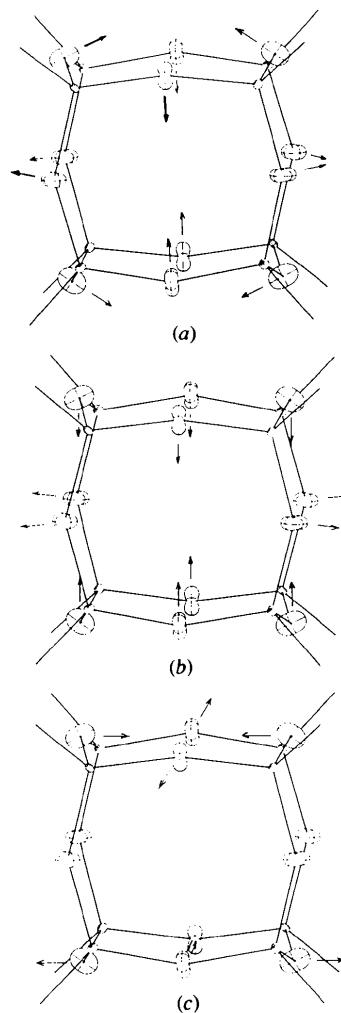


Fig. 5. Schematic representation of the deformation modes of an $m\bar{3}m$ -symmetric Si_8O_{12} -fragment built from rigid SiO_3 groups which are joined flexibly across the O atoms. (a) A_{2g} deformation: can be described as a correlated rotation of the SiO_3 groups about the exocyclic bonds. (b) E_g deformation (one component only): essentially a compression along the vertical axis. (c) T_{2g} deformation (one component only): can be described as a compression/elongation of the O_4 squares of the top and bottom faces, which is antisymmetric relative to the horizontal mirror plane.

Three modes of distortion were found to account for 92% of all distortions present in the sample (Bieniok & Bürgi, 1994); shown schematically in Figs. 5(a) and 5(b). They correspond to an A_{2g} and a pair of E_g distortions of a symmetric Si_8O_{12} fragment. The former is a cooperative rotation of rigid SiO_3 fragments about the R -Si axes, changing mainly the Si—O torsion angles; the latter is essentially an expansion/compression along the fourfold axes of the reference structure; it deforms primarily the Si—O—Si bond angles. From spectroscopy the force constants for Si—O—Si angle bending and Si—O torsional deformation were found to be small, much smaller than those for O—Si—O bending and Si—O stretching (Bärtsch, Bornhauser, Calzaferri & Imhof, 1994).

The following model of molecular flexibility is consistent with all the above observations about static molecular deformations: The SiO_3 fragments in the $\text{H}_8\text{Si}_8\text{O}_{12}$ cage are essentially rigid, but joined flexibly by O atoms which act as hinges or ball joints. The 20-atom fragment Si_8O_{12} has $3 \times 20 - 6 = 54$ degrees of freedom. For rigid SiO_3 fragments, 24 Si—O distances and 24 O—Si—O angles may be taken as fixed. A symmetry analysis shows that the remaining six degrees of freedom transform as A_{2g} , E_g and T_{2u} irreducible representations of $m\bar{3}m$ [A_g , E_g and T_u of $m\bar{3}$; Figs. 5(a)–(c)]. The A_{2g} and E_g molecular deformations are very similar to those identified in the statistical analysis of 16 Si_8O_{12} fragments (Bieniok & Bürgi, 1994).

In summary, the nonrigidity of $\text{H}_8\text{Si}_8\text{O}_{12}$ has been established from the observed U 's of Si and O. The intramolecular deformation modes have been identified from (1) a statistical analysis of the equilibrium structures of $\text{R}_8\text{Si}_8\text{O}_{12}$ molecules and (2) a symmetry analysis of the deformation modes of a Si_8O_{12} fragment built from rigid SiO_3 groups, joined flexibly across the O atoms.

4.2. Interpreting the anisotropic displacement parameters of $\text{H}_8\text{Si}_8\text{O}_{12}$ measured at 100 K

From §3 there are two options to interpret the anisotropic displacement parameters. One is to determine Σ' [see equation (12)], taking into account translation, libration, angle deformation at oxygen (two E_g and three T_u deformations) and torsion about the Si—O bonds (one A_g deformation). From Σ' the normal vibrations may be calculated using (10), provided all elements of Σ' can be obtained from the least-squares calculation (13).

An alternative is to use the force constants for Si—O stretching, O—Si—O bending, H—Si stretching and H—Si—O bending obtained from a vibrational normal coordinate analysis (Bärtsch, Bornhauser, Calzaferri & Imhof, 1994), to systematically vary the force constants for Si—O—Si bending and Si—O torsion and to calculate the eigenvalues and eigenvectors according to (6). From the eigenvectors are calculated the contributions to the atomic U 's which are due to the internal motions alone. From these, the ΔU 's along internuclear

Table 3. Frequencies and force constants for the low-energy normal modes from mean square amplitudes and vibrational normal coordinate analysis

Mode	100 K	10 K*	IR/Raman†
A_g (cm^{-1})	49	(49)	57‡
E_g (cm^{-1})	75	(75)	84§
T_u (cm^{-1})	62	(62)	68‡
$L(T_g)$ (cm^{-1})	47,47,48	45,45,37	—
$T(T_u)$ (cm^{-1})	32,32,32	19,19,17	—
$f(\text{Si—O—Si})$ (mdyn Å)	0.077	—	0.091
$f(\text{SiO—SiO})$ (mdyn Å)	0.0034	—	0.0040

* Frequencies determined from mean square amplitudes at 100 K predict the ΔU_{SiO} values at 10 K, see Table 1.

† From Bärtsch, Bornhauser, Calzaferri & Imhof (1994).

‡ Calculated.

§ Observed.

vectors are obtained (16) and compared with the experimental quantities (Raselli, 1991).

For the present analysis of $\text{H}_8\text{Si}_8\text{O}_{12}$, the latter alternative was chosen, because ΔU values tend to be less affected by systematic error than the U 's themselves (Chandrasekhar & Bürgi, 1984). The calculations were performed with a locally modified version of the program ASYM20 (Hedberg & Mills, 1993).

The Si—O—Si bending and the Si—O torsion force constants were fitted to reproduce the three nonbonded ΔU values measured at 100 K. It is pleasing to note that the same force constants predict corresponding values obtained at 10 K (Table 1).

As a further test of these calculations, the observed anisotropic displacement parameters were corrected for all internal motion according to

$$\Delta U = U_{\text{obs}} - U(\text{internal motion}), \quad (20)$$

and the residuals ΔU subjected to rigid body analysis. The translational amplitudes are now substantially smaller, all e.s.d.'s have decreased and the goodness-of-fit quantities are significantly better (Table 2), although not completely satisfactory.

Finally, in Table 3, the frequencies of intramolecular motion obtained from anisotropic displacement parameters are compared with those measured by IR and Raman spectroscopy or calculated from (6). The spectroscopic values are bigger by 8 cm^{-1} on average, but their ordering is the same as that obtained from anisotropic displacement parameters.

Correspondingly, the force constants from anisotropic displacement parameters are somewhat smaller than those from spectroscopy. The librational and translational frequencies may only be compared between the two temperatures. The agreement is better for libration than for translation. This is not entirely unexpected since the two measurements were performed on different crystals with different instruments (Törnroos, 1994) and corresponding systematic differences between anisotropic displacement parameters tend to accumulate in T (Chandrasekhar & Bürgi, 1984). It is too early to say,

however, whether the difference must be attributed entirely to systematic errors in the anisotropic displacement parameters or whether the model used for their interpretation is also insufficient.

5. Postscript

Given that this account was written for the symposium 'New Trends in Small Molecule Crystallography', it seemed admissible to present some ideas and their possible consequences, without providing at the same time a comprehensive test of their feasibility and an exhaustive documentation of difficulties. It nevertheless seems to emerge that an uncompromising application of normal coordinate analysis – either in vibrational frequency or in mean square amplitude form, or in a combination of both forms – will lead to a better understanding of anisotropic displacement parameters, to a visualization of the cooperative displacements of atoms in molecules which are considered to be embedded in the mean field of their crystalline environment, and to an appreciation of the forces governing such motion. Combining frequency with mean square amplitude data seems particularly promising, because the two types of data are complementary: high frequency vibrations are relatively easy to measure and to assign by spectroscopic techniques; they are least affected by the molecular environment (Decius & Hexter, 1977) and their contribution to the mean square amplitudes is relatively small (except for light atoms such as hydrogen). Low-frequency vibrations are more difficult to obtain from spectroscopy, but are the main contributors to the mean square amplitudes and are therefore more easily accessible from Bragg scattering experiments.

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